

Excitation Energy Dependent Soft X-ray Emission Experiments on Some Complex Oxides, and Sulfides and Irradiated Polymers

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INTRODUCTION

We are in the midst of a new revolution in materials development, and the ability to measure their electronic properties by a photon probe. Of course the copper oxide perovskites and related compounds have been of intense interest for years because of the superconducting nature of many of these materials. More recently colossal magnetoresistance has been observed [1] in manganese oxides. In addition many of these compounds show very interesting phase changes as a function of temperature near 100K. Furthermore it has been shown that pressure induces a phase change in the perovskite PrNiO_3 and V_2O_3 , where pressure produces an increase in the overlap of the oxygen-2p orbitals and the cation d-orbitals. [2,3] These effects were measured near the metal-antiferromagnetic insulator transition that occurs at approximately 100 K.[4] A recent use of inelastic x-ray scattering in V_2O_3 has revealed a plasmon like excitation at an energy loss of 12 eV which depends on the photon momentum transfer and another loss at 9.2 eV that is associated with a new type of valence band exciton. Measurements of this type compliment the photoemission measurements that were used to study V_2O_3 and obtain an insulating band gap of about 0.2 eV.[5] The compound V_2O_3 is important because it is an example of a classic Mott-Hubbard system in which an insulating gap forms because of short range interactions between the electrons and the atomic site. The electrical and magnetic properties of these materials are subject to delicate changes in the extent of nd orbitals as demonstrated in these experiments and more recently D.N. Argyriou *et al* [6] demonstrated that the compressibility in the Mn-O bonds of $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ change sign when traversing T_c . A detailed understanding of all these phenomena is still at the frontier of condensed matter physics.

In a broad collaboration with the Institute of Metal Physics in Yekaterinburg, Russia, Tulane University, University of Tennessee, the Center for Advanced Microstructures and Devices at LSU, and Lawrence Berkeley Laboratory, we have obtained X-ray fluorescence spectra and calculated the electronic structure of a number of compounds, including superconductors, magnetic materials, layered compounds having a perovskite structure, and irradiated polymer films in order to elucidate the electronic properties of some of these advanced materials. The excitation energy dependent measurements for a number of sample systems are summarized in the following paragraphs. Several of the materials studied will be highlighted in separate abstracts.

RESULTS:

1. Superconductors

The excitation energy dependence of the O K α X-ray emission spectra (2p \rightarrow 1s transition) of the copperless oxide superconductor Sr₂RuO₄ has been measured near the O 1s absorption threshold at excitation photon energies between 529.2 and 543.7 eV.[7] Spectral features in the emission spectra are attributed to the excitation of inequivalent O(1) in-plane and O(2) apical oxygens. From these spectra we were able to deduce the distribution of the corresponding O 2p-density of states and compare our results with band structure calculations. We found a marked difference in the electronic structure of Sr₂RuO₄ and superconducting cuprates in that O(1) 2p-states are mixed with d(t_{2g})-states in Sr₂RuO₄ forming p-bonds.

2. Layered compounds having a perovskite structure

The sulfur L_{2,3} X-ray emission spectra (3s \rightarrow 2p transitions) of BaCo_{1-x}Ni_xS₂ layered compounds having a perovskite structure were measured[8] near the 2p-threshold of sulfur at photon energies between 163.5 and 173.5 eV. The data are compared with soft x-ray photoemission (XPS) spectra and FLAPW band structure calculations of BaNiS₂ and BaCoS₂. By using various energies to excite the S L_{2,3} emission, the distribution of S(2) and S(1)+S(2) 3s 3d partial density of states in the valence band of BaCo_{1-x}Ni_xS₂ compounds was mapped. Our spectra and calculations yielded evidence that Sulfur 3d-states participate in chemical bonding by hybridizing with Ni 3d-states.

3. Metal sulfides

The sulfur L_{2,3} X-ray emission spectra of the transition metal sulfides, CuS, FeS₂, and CuFeS₂ were excited by tunable synchrotron radiation near the sulfur 2p threshold.[9] An excitation energy dependence of the sulfur L_{2,3} XES is only observed for CuS, and it is attributed to the presence of inequivalent sulfur atoms in CuS. Two thirds of the sulfur atoms form S₂ dimers (as in FeS₂) while the remaining sulfur atoms remain as monomers (as in CuFeS₂), in accordance with XPS measurements and band structure calculations,[9] we have shown that selective excitation of valence band emission spectra can be used to determine the atom-decomposed partial density of states for inequivalent sites in solids, occupied by chemically identical species.

4. Electronic density of states of Eu_{1-x}Co_xMnO₃

The results of measurements of XPS, O 1s total fluorescence yield and fluorescence x-ray emission valence band spectra (O K and Mn L_{2,3}) near the O 1s and Mn 2p- absorption thresholds in the compound Eu_{1-x}Co_xMnO₃ are compared with LSDA and LDA+U band structure calculations.[10] We find that LSDA method is more accurate than the LDA+U approach for describing the spectroscopic properties of the orthorhombic EuMnO₃ system.

5. Emission from annealed sulfur compounds

Sulfur L_{2,3} X-ray emission spectra, excited by synchrotron radiation at energies near the sulfur 2p threshold at photon energies between 163-165 eV, have been obtained[11] in samples containing 240 ppm S in Ni, annealed to 400-700 C. We found that S L_{2,3} x-ray emission spectra (XES) of S-impurity atoms in Ni show a fine structure which can be simulated by a superposition of the sulfur L_{2,3} spectrum from nickel sulfide and from pure sulfur. This suggests that the sulfur atoms are present after annealing both in solid solution and in clusters where they form S-S bonds. The variation of temperature and time of annealing (T=400 °C for 1 hr and T=700 °C for 2 hrs) leads to a redistribution of the intensity of the S L_{2,3} x-ray emission valence band spectra,

which can be attributed to changes in the number of S-Ni and S-S bonds in accordance with the limit of sulfur solubility at these temperatures.

6. Carbon K α emission from PI and PCS films

Fluorescent ultra-soft C K α x-ray emission spectroscopy has been used[12] for the characterization of bonding configurations of C-atoms in polyamide (PI) films irradiated with N $^{+}$ and Ar $^{+}$ ions with doses ranging from 1×10^{14} to 1×10^{16} ions/cm 2 , and polycarbosilane (PCS) films after annealing and irradiation with C $^{+}$ ions to a concentration of 5×10^{15} ions/cm 2 . We found that the fine structure of C K α x-ray emission of PI changes for concentrations greater than 1×10^{14} ions/cm 2 , which we attribute to the degradation of polyamide films and creation of carbon clusters within the material. The width of the band gap for the heavily irradiated PI films, as determined from high-energy decrease of C K α x-ray emission, decreases with increasing ion dose. This behavior correlates with an increase of conductivity due to polymer carbonization in these films. We find that the bonding configuration of C-atoms of PCS films after irradiation with C $^{+}$ ions at 5×10^{15} ions/cm 2 is close to that of a diamond-like films, while films receiving a treatment of annealing in addition to irradiation have an electronic structure more like silicidated graphite. Our observations suggest that annealing a PCS film at a temperature 1000 °C leads to the conversion of the annealed polycarbosilane films to a ceramic with a structure similar to that of amorphous Si $_{0.77}$ C $_{0.23}$:H.

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